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Modeling purification of phosphoric acid contaminated with cadmium by liquid-liquid extraction

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Abstract

Phosphoric acid production is considered as second worldwide after that of sulphuric acid. It is an important and necessary intermediate chemical compound in sensitive industrial fields such as the fertilizers, detergents, food, pharmaceutical industries. Its main production is through the wet process which is responsible for the presence of various impurities like metallic cations such as Pb^{2+}, Cd^{2+}, Mg^{2+}, etc, initially contained in the phosphate rocks. Indeed many techniques for the purification of phosphoric acid have been developed. In this work the modeling of the purification of phosphoric acid by liquid-liquid extraction was considered. The model was tested on Cd^{2+} as contaminant and di (2ethylhexyl) dithiophosphoric acid diluted in dodecane as complexing agent. The results obtained from a parametric study investigating the effect of the initial concentrations of phosphoric acid and that of the complexing agent, are reported.

Keywords: Phosphoric acid, Solvent extraction, Purification, Wet process, Dodecane.

1. Introduction

Phosphoric acid is an important intermediate in the synthesis of fertilizer and in the development of pure products for the food industry and surface treatment. It is mainly obtained through the attack of phosphate rock with sulfuric acid. Its quality depends greatly on the P_2O_5 rock content and nature of the present impurities, among which some can be recovered like uranium, rare earth, etc. but others are rather not desirable like heavy metal cations or organic pollutants, and hence must imperatively be eliminated.

In fact the growing concern for researchers regarding the contamination of the phosphoric acid has resulted in great efforts to develop different techniques of purification of the phosphoric acid, by eliminating the present impurities. One can cite different routes like crystallization, evaporation, fixation

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on land filtration, precipitation and liquid-liquid which is the main interest of the present study. However in the literature, most of the reported research works are of an experimental nature [1, 2, 3] and just few are based on modeling. This has been then a stimulating factor to attempt a modeling of this complex process which involves simultaneously chemical and physical equilibria.

2. Thermodynamic model

A priori a general model for the purification of phosphoric acid by liquid-liquid extraction should be based on the following steps:

1. Calculation of molar or mass fractions of the different species present in both phases by the use of a complexation model that take into account all the occurring chemical reactions which lead the system to an equilibrium state;
2. Resolution of the phase equilibria problem since a liquid-liquid extraction operation is basically a mass transfer process to lead to the equality of the activities for each component in each phase.
3. The above step 2 requires the use of a thermodynamic model like the modified UNIQUAC model (modified to handle the presence of electrolytes) which in turn requires interaction parameters which are calculated from the results obtained in the complexation step.

Calculation of phase equilibrium: using the results obtained from step 3, it should be noted that in this stage one must reach almost the same fractions obtained in step 1in order to confirm the reliability of the model used in this study.

2.1. Step 1: Complexation model

The model proposed by Devore [4] assumed that the electrolyte dissociates leading to the formation of a complex (or more complex) according to the following reactions:

$$A \leftrightarrow B + C \qquad K_1 \tag{1a}$$

$$B \leftrightarrow D + C \qquad K_2 \tag{2a}$$

$$F \leftrightarrow G + H \qquad K_i \tag{3a}$$

with $K_1, K_2, \ldots\ldots K_i$ expressing the equilibrium constants of the dissociation reactions.

The initial concentrations of the different species in the reaction mixture are specified, while those resulting from the dissociation of phosphoric acid are considered as zero. If $[A]^i$, $[B]^i$I…. represent the molar concentrations to the i^{eme} iteration, the values of the next iteration (i +1) will be calculated from the equilibrium equations for example for the following reaction:

	A	↔	B	+	C
i^{eme} iteration	$[A]^i$		$[B]^i$		$[C]^i$
(i+1) iteration	$[A]^i - \Delta$		$[B]^i + \Delta$		$[C]^i + \Delta$

We put $[A]^{i+1} = [A]^{i} - \Delta$ (1b)

$$[B]^{i+1} = [B]^{i} + \Delta \quad (2b)$$

$$[C]^{i+1} = [C]^{i} + \Delta \quad (3b)$$

where Δ is concentration step.
The equilibrium constant in the iteration (i) is given by:

$$K_i = \frac{([c]^{i}-)([B]^{i}-)}{[A]^{i}-} \quad (4b)$$

By neglecting the terms of Δ whose exponents greater than 1, gives:

$$\Delta_1 = \frac{K_1[A]^{i}]-[B]^{i}[c]^{i}}{[c]^{i}+[B]^{i}+K_1} \quad (5b)$$

The concentrations of the species are adjusted several times during one iterative cycle. If a negative concentration is obtained for a reaction, it is skipped until the next iteration.

The present case concerns the study of the purification of phosphoric acid contaminated with cadmium, di (2-ethylhexyl) dithiophosphoric acid (D2EHDTPA) as complexing and dodecane as a diluent. The experimental study was conducted by Touati et al [5].

The different chemical equilibrium taking places in the aqueous phase are the following dissociation [6] and complexation [5] reactions:

$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$ $K_1 = 7.107\ 10^{-3}$ (R1)

$H_2PO_4^- \leftrightarrow HPO_4^{-2} + H^+$ $K_2 = 4.275\ 10^{-7}$ (R2)

$HPO_4^{-2} \leftrightarrow PO_4^{-3} + H^+$ $K_3 = 1.15\ 10^{-12}$ (R3)

$H_3PO_4 + H_2PO_4^- \leftrightarrow H_5P_2O_8^-$ $K_4 = 1.263$ (R4)

$H^+ + H_5P_2O_8^- \leftrightarrow H_6P_2O_8$ $K_5 = 0.3$ (R5)

$H_2O \leftrightarrow H^+ + OH^-$ $K_6 = 10^{-14}$ (R6)

$Cd^{2+} + 2\mathrm{HR} \leftrightarrow CdR_2 + 2H^+$ $K_7 = 11\ 10^{6}$ (R7)

Applying the previously described model, one gets:

$$\Delta_1 = \frac{K_1[H_3PO_4]-[H_2PO_4^-][H^+]}{[H_2PO_4^-]+[H^+]+K_1} \quad (1)$$

$$\Delta_2 = \frac{K_2[H_2PO_4^-]-[HPO_4^{-2}][H^+]}{[HPO_4^{-2}]+[H^+]+[K_2]} \quad (2)$$

$$\Delta_3 = \frac{K_3[HPO_4^{-2}]-[PO_4^{-3}][H^+]}{[PO_4^{-3}]+[H^+]+K_3} \quad (3)$$

$$\Delta_4 = \frac{K_4[H_3PO_4][H_2PO_4^-]-[H_5P_2O_8^-]}{1+K_4[H_3PO_4]+K_4[H_2PO_4^-]} \quad (4)$$

$$\Delta_5 = \frac{K_5[H^+][H_5P_2O_8^-]-[H_6P_2O_8]}{1+K_5[H^+]+K_5[H_5P_2O_8^-]} \quad (5)$$

$$\Delta_6 = \frac{K_6-[H^+][OH^-]}{K_6+[H^+]+[OH^-]} \quad (6)$$

$$\Delta_7 = \frac{K8[Cd^{2+}][HR]^2-[CdR_2][H^+]^2}{K_8[HR]^2+4K_8[Cd^{2+}][HR]+4[H^+][CdR_2]+[H^+]^2} \quad (7)$$

The concentrations and mole fractions of different species in the mixture are calculated by solving equations (1-7) simultaneously.

2.2. Steps 2 and 3: phase equilibria

For the calculation or prediction of liquid-liquid equilibria based on the estimation of activity coefficients requires the use of specific models, chosen according to the properties of the considered mixtures (electrolytes, no electrolytes, hydrocarbons, polymers, etc ....). Among these models, one can cite NRTL, UNIFAC and UNIQUAC. In the present study the calculation of the interaction parameters and hence the calculation of the activity coefficients is carried out by means of the modified UNIQUAC model.

Modified UNIQUAC model

According to this model the activity coefficient is given as follows [7]:

$$Ln\gamma_n = Ln\gamma_n^{DH} + Ln\gamma_n^{C} + Ln\gamma_n^{R} \quad (8)$$

$$Ln\gamma_b^{*}=Ln\gamma_b^{*,DH}+Ln\,\gamma_b^{*,c}\text{n}+Ln\gamma_b^{*,R} \quad (7)$$

n and b denote the solvent and the ion, respectively. $Ln\gamma_n^{DH}, Ln\gamma_n^{C}, Ln\gamma_n^{R}$ are the Debye-Huckel, the combinatorial and the residual contributions to the activity coefficient of solvent n or ion b, respectively and are expressed as follows:

- **The Dubye-Huckel term**

$$ln\gamma_n^{DH} = M_n\frac{2A}{b^s}(1+\mathrm{b}I^{1/2}-1/(1+\mathrm{b}I^{1/2})-2\ln(1+\mathrm{b}I^{1/2})) \quad (9)$$

$$ln\gamma_b^{*,DH} = -Z_b^2 A \frac{I^{1/2}}{1+bI^{1/2}} \quad (10)$$

- **The combinatorial term**

$$Ln\gamma_n^c = Ln\frac{\phi_n}{x_n} + 1 - \frac{\phi_n}{x_n} - \frac{1}{2} z q_n \left(Ln\frac{\phi_n}{\theta_n} + 1 - \frac{\phi_n}{\theta_n}\right) \quad (11)$$

$$Ln\gamma_b^{*,c} = Ln\frac{\phi_b}{x_b} - \frac{\phi_b}{x_b} - Ln\frac{r_b}{r_w} + \frac{r_b}{r_w} - \frac{1}{2} z q_b \left(Ln\frac{\phi_b}{\theta_b} - \frac{\phi_b}{\theta_b} - Ln\frac{r_b q_w}{r_w q_b} + \frac{r_b q_w}{r_w q_b}\right) \quad (12)$$

where r_w, q_w and are the parameters of area and volume of surface and Z = 10. θ_b, ϕ_b and ϕ_n are calculated as follows:

$$\theta_i = \frac{x_i q_i}{\sum_l x_l q_l} \quad (13)$$

$$\phi_i = {x_i r_i}/{\sum_l x_l r_l} \quad (14)$$

- **The residual term**

$$Ln\gamma_n^R = q_n \left(1 - Lns_n - A_n - \frac{2}{T} B\right) \quad (15)$$

$$Ln\gamma_b^{*,R} = q_b \left(-Lns_b - A_b + \frac{1}{T}(D_b + E_b - 2B) + Ln\Psi_{w,b}^{\infty,w} + \Psi_{b,w}^{\infty,w}\right) \quad (16)$$

where:

$$s_l = \sum_K \theta_k \Psi_{kl} \quad (17)$$

$$C_{kl} = \frac{\Psi_{kl}}{s_l} \quad (18)$$

$$A_k = \sum_l \theta_l C_{kl} \quad (19)$$

$$D_b = \sum_{i \neq b} \sum_m \theta_i^2 \theta_m \delta_{ib,m} (C_{im} + C_{mi}) \quad (20)$$

$$E_b = \sum_m \theta_m f_{bm} (C_{bm} + C_{mb}) \quad (21)$$

$$f_{bm} = \theta_b \sum_{i \neq b} \delta_{bi,m} \theta_i \quad (22)$$

$$B = \sum_i \theta_i E_i \quad (23)$$

$\Psi_{w,b}^{\infty,w}$ and $\Psi_{b,w}^{\infty,w}$ are the values of $\Psi_{w,b}$ and $\Psi_{b,w}$ in water pure. $\sum_k$, $\sum_1$ are sums over all species in the system.

$$\Psi_{Kl} = \exp\left(-\frac{a_{kl}}{T}\right) \quad (24)$$

In this case a_{kl} is the interaction parameter between species k and l.

A priori, the interaction parameters of the modified UNIQUAC model can be determined from the minimization of an objective function that can be written as follows:

$$F=\sum_i \sum_j [\ln (\gamma_j x_j)^I - \ln(\gamma_j x_j)^{II}]^2 \quad (26)$$

$(\gamma_j x_j)^I$ and $(\gamma_j x_j)^{II}$ are the activities of the constituent j in the two phases for each extension line. The objective function F is minimized by the simplex method of optimization developed by Nelder and Mead 1965 [4].

3. Results and discussion

The proposed model is tested for the purification of phosphoric acid contaminated with Cd^{2+} ion, the complexing agent is di (2-ethylhexyl) dithiophosphoric acid (D2EHDTPA) and dodecane as diluent (Cd^{2+}, H_3PO_4, $D_2EHDTPA$). A priori, for a given initial concentration of $D_2EHDTPA$, the total amount of complex formed should be calculated. It is calculated through the value of complexation ratio R that is defined as [6] the total amount of complex formed over that of initial free Cd^{2+} (before complexation). In other words, R gives an idea of the extent of the complexation.

To check the accuracy of the computer code developed the experimental results were compared with those calculated by the model and Figure 1 shows such a comparison where it can be seen that the agreement is excellent and the model can be regarded as reliable.

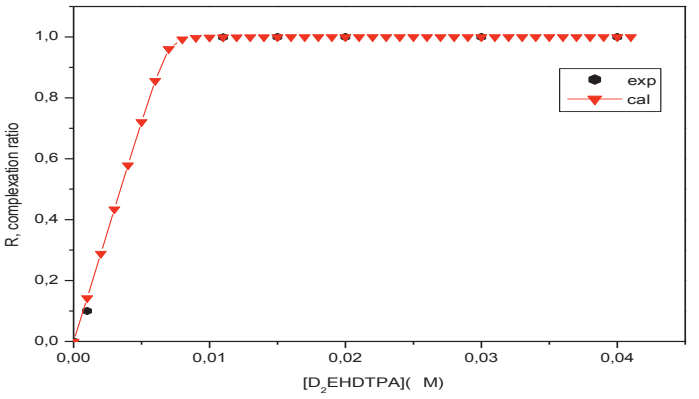

Figure1. Comparison between the experimental data and calculated values

Figure 2 shows that for a small amount of complexing agent, a rapid increase in the ratio of complex is noted and particularly for low concentrations of the metal.

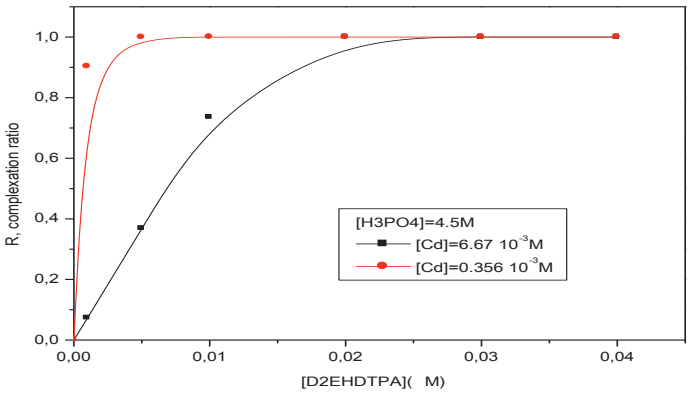

Figure 2. Effect of concentration of complexing agent on the report of complexation for different concentrations of the metal [Cd^{2+}]: 6.67 10^{-3}M, 0356 10^{-3} and [H_3PO_4]: 4.5M

The effect of the initial concentration of phosphoric acid on R has also been investigated.
Figure 3 shows the effect of initial concentration of phosphoric acid on the report of complexation. Increasing the acidity of phosphoric acid, will decrease the ratio of complexation, and this for all concentrations of the complex. This can be explained by the fact that complex formation is favoured with increasing concentration of phosphoric acid so this can be used as a means to select the concentration of the acid which promotes the formation of the complex and this is in a good agreement with experimental results [8].

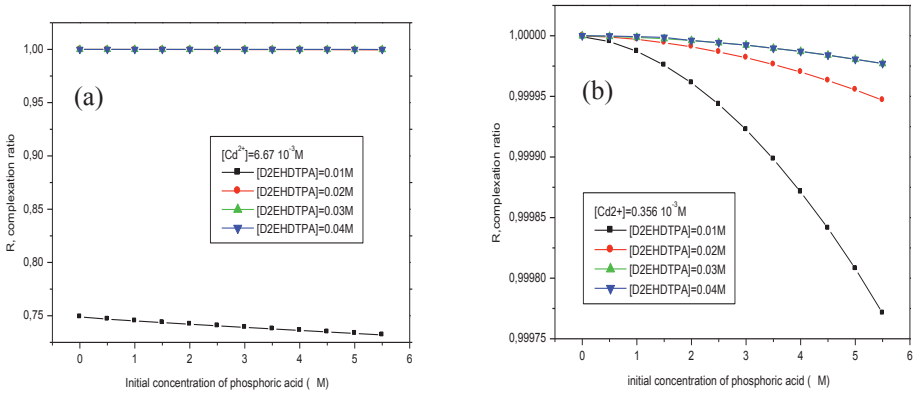

Figure 3. Effect of initial concentration of phosphoric acid on the report of complexation for different concentrations of the complex [D_2EHDTPA]: 0.01M, 0.02M, 0.03M, 0.04M and different concentrations of the metal: (a) 6.67 10^{-3}M (b) 0356 10^{-3}M.

The amount of the complex remaining in the aqueous phase after separation has been calculated using the above approach and the experimental data reported in [5]. Applying the thermodynamic approach

described above, a huge matrix of interaction parameters has been obtained as shown in tables 1, 2 and 3 where all the values have been used to simulate the distribution of different species between the aqueous and the organic phases.

Table 1. UNIQUAC interaction parameters $a_{ij}(k)$.

	H_2O	Dodecane	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H^+
H_2O	0	20.493	10.975	67.849	19.956	69.848	94.796
Dodecane	141.841	0	11.687	23.334	41.919	103.293	-117.273
H_3PO_4	-250.083	14.586	0	620.662	541.570	250.169	241.238
$H_2PO_4^-$	504.574	3908.235	8199.470	0	798.858	2412.628	250.182
HPO_4^{2-}	487.591	20.002	240.251	250.262	0	26.810	10.171
PO_4^{3-}	125.155	397.107	3526.921	793.463	250.178	0	313.063
H^+	2260.770	617.173	268.103	7006.548	250.082	-910.955	0
OH^-	445.543	49.016	248.831	59.728	250.153	250.178	992.039
$H_5P_2O_8^-$	301.800	229.192	298.116	540.576	480.502	730.803	560.199
$H_6P_2O_8$	150.113	110.035	801.851	250.474	133.164	855.629	465.566
Cd^{2+}	50.047	4096.730	25.009	601.154	800.983	174.346	58.467
HR	400.316	510.183	275.290	551.072	902.723	637.526	356.680
CdR_2	1319.01	610.198	24.928	911.733	601.097	25.038	10.011
SO_4^{2-}	39.946	250.082	981.436	310.560	401.753	2223.532	421.807

	OH^-	$H_5P_2O_8^-$	$H_6P_2O_8$	Cd^{2+}	HR	CdR_2	SO_4^{2-}
H_2O	35.923	71.848	12.973	72.849	12.973	2.993	28.942
Dodecane	240.628	3420.683	326.647	480.583	123.141	225.234	199.134
H_3PO_4	983.124	410.436	-215.223	602.155	511.651	404.616	58.467
$H_2PO_4^-$	3921.392	510.183	24.388	5.436	17.720	362.209	1237.699
HPO_4^{2-}	458.524	341.901	140.379	30.515	62.472	25.038	10.011
PO_4^{3-}	359.312	298.341	9811.444	3112.782	4016.845	213.253	4219.217
H^+	592.587	243.075	904.345	527.010	644.785	357.692	365.701
OH^-	0	904.031	191.197	-110.039	904.027	200.072	300.335
$H_5P_2O_8^-$	891.967	0	263.184	65.694	952.096	460.276	24.928
$H_6P_2O_8$	445.543	254.862	0	-620.662	510.536	1026.043	250.182
Cd^{2+}	501.570	305.138	891.954	0	280.274	250.169	250.183
HR	48.084	20.002	233.243	293.310	0	250.082	250.183
CdR_2	15.026	500.229	35.911	800.472	250.178		350.259
SO_4^{2-}	228.435	176.201	268.103	700.391	250.082	1000.058	0

Table 2. $\delta_{ij,m}$ parameters (k) for m=H_2O

	H_2O					
	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H^+	OH^-
H_3PO_4	0	520.503	250.082	910.352	527.010	647.788
$H_2PO_4^-$	250.153	0	250.178	100.036	98.101	20.002
HPO_4^{2-}	300.118	60.017	0	50.018	30.004	560.199
PO_4^{3-}	150.113	1511.653	810.861	0	2553.121	136.168
H^+	250.169	29.934	914.043	410.436	0	25.009
OH^-	90.043	720.773	250.169	250.183	400.316	0
$H_5P_2O_8^-$	48.084	110.107	243.254	30.0149	250.082	250.183
$H_6P_2O_8$	25.038	10.011	15.026	500.229	35.911	800.472
Cd^{2+}	310.560	401.753	21.033	421.807	228.435	611.166
HR	250.083	910.352	527.010	64.124	37.322	365.701
CdR_2	250.178	100.036	94.096	110.107	110.039	20.015
SO_4^{2-}	60.017	50.018	30.004	560.199	90.032	227.142

H_2O						
	$H_5P_2O_8^-$	$H_6P_2O_8$	Cd^{2+}	HR	CdR_2	SO_4^{2-}
H_3PO_4	357.692	365.701	44.080	49.016	248.831	600.337
$H_2PO_4^-$	110.039	10.003	200.072	300.335	3024.928	229.192
HPO_4^{2-}	90.032	26.910	657.379	91.097	460.276	250.183
PO_4^{3-}	855.629	461.561	444.542	240.846	660.710	590.625
H^+	601.154	80.151	74.235	579.071	50.061	305.138
OH^-	510.183	241.252	551.072	902.723	36.841	356.680
$H_5P_2O_8^-$	0	1319.010	610.198	24.928	911.733	601.096
$H_6P_2O_8$	250.178	0	350.259	39.946	250.083	981.435
Cd^{2+}	268.103	700.391	0	250.083	100.013	59.969
HR	44.080	49.016	248.831	0	600.337	29.904
CdR_2	200.072	30.024	321.823	28.965	0	300.118
SO_4^{2-}	657.379	10.005	460.277	250.182	150.113	0

Table 3. $\delta_{ij,m}$ parameters (k) for m=dodecane

Dodecane						
	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H^+	OH^-
H_3PO_4	0	110.035	-802.852	250.474	13.024	855.629
$H_2PO_4^-$	250.182	0	70.070	-556.763	987.010	99.853
HPO_4^{2-}	189.374	300.343	0	47.053	23.0263	14.0160
PO_4^{3-}	10.011	20.022	84.096	0	865.991	632.724
H^+	52.059	40.045	98.112	35.040	0	79.090
OH^-	423.484	368.421	269.308	248.284	321.367	0
$H_5P_2O_8^-$	47.053	23.026	14.016	159.182	32.036	36.041
$H_6P_2O_8$	84.096	24.928	150.113	110.035	801.851	250.474
Cd^{2+}	-620.662	580.614	104.619	260.194	420.467	2094.410
HR	101.115	20.002	3.003	4.004	5.005	6.006
CdR_2	660.710	590.625	250.169	29.934	914.042	410.436
SO_4^{2-}	50.060	1938.642	1889.343	1378.807	1689.193	2359.682

Dodecane						
	$H_5P_2O_8^-$	$H_6P_2O_8$	Cd^{2+}	HR	CdR_2	SO_4^{2-}
H_3PO_4	46.082	44.080	24.598	70.041	60.029	250.169
$H_2PO_4^-$	574.749	244.817	238.835	2388.344	106.532	1033.400
HPO_4^{2-}	159.182	32.036	36.041	1.001	147.168	12.013
PO_4^{3-}	95.108	14.016	45.051	250.286	74.084	15.017
H^+	100.114	20.022	45.051	30.034	80.091	156.178
OH^-	148.169	75.085	42.048	159.182	78.089	322.369
$H_5P_2O_8^-$	0	1.001	147.168	12.013	10.011	20.022
$H_6P_2O_8$	133.164	0	855.620	358.410	445.948	214.816
Cd^{2+}	25.009	15.557	0	147.366	347.998	59.468
HR	7.008	8.009	9.010	0	444.542	240.846
CdR_2	25.009	601.154	80.151	74.235	0	579.071
SO_4^{2-}	2456.991	218.750	4103.196	578.103	24.027	0

Table 4 presents a comparison between the values of fractions of solute in the two phases obtained from the complexation model and that obtained by the model balances (using equation UNIQUAQ modified the purpose of determining the activity coefficient).

Table 4.

Table 4. Comparison between the two calculation models

	Fraction obtained by the complexation model (f_1)	Fraction obtained by the equilibrium model(f_2)	Error %
X1	$2.7796018\ 10^{-6}$	$2.6509272\ 10^{-6}$	4.63
X2	$3.7509361\ 10^{-3}$	$3.5189835\ 10^{-3}$	6.18

With : X1 : metal fraction in the aqueous phase after equilibrium

X2 : fraction of the complex in the organic phase after equilibrium.

Error : error between the two models is given by

$$Error(\%) = \frac{|(f1 - f2)| * 100}{f1}$$

4. Conclusion

Modeling of chemical equilibria was used to determine the fractions of the different species present in the solution of phosphoric acid. Process modeling of liquid-liquid extraction allowed the determination of interaction parameters and also checking the reliability of model developed in this study. In conclusion, this study should be seen as an attempt to model the liquid-liquid extraction starting from purely theoretical considerations of thermodynamics and mass transfer.

5. References

[1] K. Nazri, A. Ghadiri, H. Babaie, Elimination of cadmium from wet process phosphoric acid with alamine 336, Minerals Engineering 18pp 1233-1238, 2005;

[2] J.Stas, D. Pareau, A. Chesne, G. Durand, Extraction du cadmium par l'acide bis-2-ethylhexylphosphorique et étude de sa complexation par les ions phosphate, Bull Soc Chim Fr 127, pp 360-366, 1990 ;

[3] A.Mellah, D.Benachour, The solvent extraction of zinc and cadmium from phosphoric acid solution by di-2-ethylhexyl phosphoric acid in kerosene diluents, Chemical Engineering and Processing 45, pp 684-690;

[4] J.A.Devore, A simple numerical method for solving complex equilibria, J. Chem Educ, 65, pp 868-870, 1988;

[5] M. Touati, M. Benna-Zayani, N.Kbir-Ariguib , M.Trabelsi-Ayadi, A.Buch, J.L. Grossiord, D.Pareau and M.Stambouli, Extraction of cadmium (II) from phosphoric acid media using the di(2-ethylhexyl)dithiophosphoric acid ($D_2EHDTPA$): Feasibility of a continuous Extraction-stripping process Hydrometallurgy, 95, pp135–140, 2009;

[6] A.Bendada, A.Meniai, Modling of phosphoric acid by liquid-liquid extraction, Chem. Eng, 24, pp 1273-1280, 2001.

[7] B.Sander, A.Fredenslund, P.Rasmussen, Calculation of vapor-liquid equilibria in nitric acid-water-nitrate salt systems using an extended UNIQUAC equation, Chemical Engineering Science, Vol.41, No.5, pp1185-1195, 1986.

[8] Mohamed El Khaiary, Extraction of Al(III) from phosphoric acid by HDDNSA,Se parathion and Purification Technology 12, pp13-16 1997.